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PROJECT NO. A-558

CHEMICAL SYNTHESES REQUIRING CRYOGENIC TEMPERATURES AS PREPARATIVE TECHNIQUES FOR HIGHLY ENDOTHERMIC CHEMICAL SPECIES

Henry A. McGee, Jr.
Project Director

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Submitted to the
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
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HENRY A. MCGEE, JR.,
Principal Investigator

(NASA GRANT NsG-123-61)

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ABSTRACT

The research supported under this NASA grant has been concerned with some of the initial phases of establishing a long range study of the broad area of low temperature chemistry at this Institute. The objectives may be categorized under two major headings; (a) instrument development centered around the mass spectrometer and (b) initial low temperature stability studies with carbene and the dihalocarbenes. This research had not been under way for long before it was very apparent that the desired experimental information would have to wait upon the successful solution to severe problems of experimental design. These problems grew from the requirements for separation and for chemical analysis of these highly reactive product mixtures which are also thermally unstable.

Since most of the reaction products or phenomena that are of interest will exist only so long as the low temperature is maintained, it is essential that chemical analyses be performed using cold materials and in manners not involving warm-up of any sort. To meet this requirement, the time-of-flight mass spectrometer has been slightly modified and a cryogenically cooled sample inlet system has been designed and constructed. In this design, the ionizing electron beam of the spectrometer makes grazing tangential incidence with the cold sample delivery system. Ozone difluoride, which is the most powerful oxidizer known and which begins to rapidly decompose above 115^{o} K, has been synthesized in this laboratory and is to be used to crystallize the operating techniques with this unique cryogenic mass spectrometer system. Since we are interested in the ultimate large scale production and utilization of the unusual

materials that can be synthesized by techniques requiring cryogenic temperatures, we have concentrated on pyrolysis for the genesis of either the species of interest or its precursor. Some high energy initiation step such as this is required since very few reactions will occur at low temperatures by merely contacting ordinary substances that have been only precooled. Free radicals or excited species are required, and we are here concerned with generating these species by processes that may, in principle, be generalized to large scale operation. Two molecular beam line-of-sight inlet systems have been designed and constructed during this grant period for studies of the effluent from pyrolysis experiments. The pyrolysis output gas becomes the cryogenic reactor input gas.

Techniques for the separation of the reaction products have also been studied. The separation process is complicated by its demanding cryogenic temperature operation with chemically highly reactive and thermally unstable materials. Since simplicity rather than efficiency seemed most desirable, a fractional freeze-out and fractional sublimation apparatus which is designed as an integral part of the cryogenic inlet system of the mass spectrometer has been developed. This permits continuous monitoring of the degree of separation that has been effected.

Because of the appearance during this grant period of results obtained by other investigators from more ordinary temperature reactivity studies and from spectroscopic studies, that diminish the feasibility of preparing carbene as a relatively pure reagent at low temperatures, we have concentrated on the dihalocarbenes. It now seems apparent that CI_2 can be made by the pyrolysis of iodoform but not from C_2I_4. CF_2 may apparently be formed from C_2F_4 which

in turn may be prepared from teflon. Apparatus for the low pressure thermal degradation of teflon is operative.

Much of the work initiated here is being continued under NASA grant NsG-337, which is concerned in addition with the reactivity of H, N, and O atoms with various simple molecules at cryogenic temperatures.

I. INTRODUCTION AND SCIENTIFIC BACKGROUND

New applications of cryogenic or very low temperature techniques have appeared at an unprecedented rate in recent years. The development of the cryotron as a memory element for computers; of bubble chambers for the observation of nuclear events; of cryopumping for producing very hard vacua; of the cryogenic gyroscope; of superconducting high field magnets, and many others have represented for their operation in fact, very significant advances in cryogenic engineering. In addition to these new developments, the low temperature physicists have continued their fundamental studies of superconductivity and superfluidity.

Unlike any of these, this research program was centered about chemical reactivity and synthesis by processes involving these very low temperatures. We have coined the word "cryochemistry" as a suitably descriptive term for chemistry and chemistry related studies such as solubility, structure, etc. at temperatures below about 100° K. In further contrast, one should recall that in the important research area of free radical stabilization, one produces a chemically labile species which is then trapped in an inert, rigid, usually glassy environment which prevents subsequent reaction. In this state the radical may be studied by a variety of physical techniques, and indeed, due to this technique much more has been learned in recent years about free radicals than was ever before possible (1)*. However, in the type of experiments of interest here, the chemical reaction in the low

*Numbers in parentheses refer to literature citations that are summarized in the Bibliography of this report.

energy environment is not retarded, but rather the observation of this reaction forms the essence of the experiment. The synthesis of previously unknown molecules, the preparation of species as condensed phases that are ordinarily observed only in the gaseous phase at very high temperatures, and the preparation of new modifications of certain elements and known compounds are among expected results from these studies. Indeed there are several examples of the accomplishment of these objectives on a scale such that they may be considered to be distinct chemical substances. Many such studies have been summarized in a review paper by McGee and Martin (2). In the following few paragraphs, some of the more significant experimental techniques are listed together with some brief comment.

Few reactions will occur at reasonable rates below 100° K by simply mixing the cold reactants (2). One of the more interesting recent studies in this regard involves the apparent synthesis of nitrosyl nitrate by Parts (3). When NO, dissolved in either of several cryosolvents, and O_2 are contacted, one observes the formation of a red, green or blue precipitate depending on the solvent and on the ratio of reactants. The blue product was formed in CH_4 solution, the green in CO solution, and they differ only by the ratio of N_2O_3 to N_2O_4 in the product. The red product may be formed in hydrocarbon solutions other than CH_4 and from infrared evidence, has been assigned the structure $ONONO_2$, nitrosyl nitrate (4). These and a very few similar studies are the beginnings of the field of solution chemistry at cryogenic temperatures. This field has great potential as a powerful technique for the illucidation of reaction mechanisms.

Combinations of low temperature trapping and the electric glow discharge in a gaseous fast flow system have been used to effect unusual chemical syntheses. The discharge may activate a single species which is then mixed with a second reactant and followed by a quench. Or the reactants may be premixed and then passed into a discharge tube that is itself maintained at a low temperature causing the products to be continuously condensed on the walls of the cold reactor. The variations on the basic idea have been numerous.

Some of the most interesting studies have been done in Russia by Kobozev and his associates (2) who have reacted hydrogen atoms with liquid ozone at 77^{o} K and have produced thereby hydrogen superperoxide, H_2O_4. During the reaction, the dark purple film of ozone becomes transparent and glassy. During warming the material evolves heat and oxygen at definite temperatures and leaves a concentrated solution of peroxide in water in the reactor. The molar ratio of evolved oxygen to remaining peroxide is always constant and is essentially unity. This was explained as the decomposition of H_2O_4 to form H_2O_2 and O_2. The low temperature product has been examined by optical spectroscopy, by electron spin resonance spectroscopy, by x-ray diffraction, and calorimetrically. There is still, however, enough disagreement on the interpretation of the nature of the low temperature material to make the preparation of H_2O_4 problematical in the minds of some, but they are in a distinct minority. During the summer of 1961, the principal investigator visited these laboratories at the University of Moscow, examined the apparatus and discussed the experiments in detail with the Russian workers.

Another example of the preparation of an unusual molecule from the combination of the gaseous discharge and cryogenic temperatures is that of the production of ozone difluoride, O_3F_2. Oxygen and fluorine gas are mixed in the stoichiometric ratio and led into a glow discharge maintained in a reactor immersed in liquid oxygen at 90° K. The blood red liquid O_3F_2 which is formed will condense on the walls of the reactor (2). This liquid is one of the most powerful oxidizers known, being more powerful than either ozone or fluorine, but it decomposes above about 115° K. Either mercury, solid NH_3, CH_4, solid N_2H_4, P, S, solid ethanol, I_2, or Br_2 when cooled to 90° K will be ignited on contact with a few drops of O_3F_2. Ultraviolet photolysis of liquid solutions of oxygen and fluroine will also produce O_3F_2 (2). This same experimental arrangement has been used in the last several months to prepare krypton tetrafluoride, KrF_4 according to one report (5). O_3F_2 has been prepared during this study for use in "proof experiments" with the cryogenic inlet to the mass spectrometer, and will be discussed further in a subsequent section of this report.

Electric arcs or sparks between metal electrodes completely submerged in low boiling solutions have been used as preparative techniques. An arc between potassium electrodes immersed in liquid argon yields a blue solid which may be a new modification of that element (2).

Flames have been operated submerged beneath the surface of low boiling liquids. Hydrogen may be ignited and will burn well beneath the surface of liquid air or liquid oxygen producing in addition to ice, reasonable quantities of NO and O_3 in the former liquid, and O_3 in the latter (2). Hydrogen peroxide is not formed in either instance. Acetylene will likewise burn

beneath liquid air producing C, CO_2, H_2O, HNO_3 and O_3. A study of this "flame synthesis"technique at cryogenic temperatures is just getting underway in this laboratory.

Finally, and of particular concern in the present NASA supported research program, synthesis techniques have been used wherein the effluent gas from a pyrolysis experiment is quenched to very low temperatures. As early as 1918, an attempt was made to prepare sulphur as a stable blue liquid (note the predicted color of the liquid) at low temperatures by quenching sulphur vapor that had been pumped through a hot tube (2). In the gas phase at moderate temperatures, sulphur exists as the dimer, S_2, in significant amounts and the attempt was to trap it in this state. These early experiments were unsuccessful, but in more recent times Rice and Sparrow and others have prepared sulphur as a purple solid by essentially the same technique (2).

Another experiment involving thermal activation, has led to the supposed production of CCl_2 by quenching to liquid air temperatures the effluent gases from the pyrolysis of CCl_4 at 1300° C (2). A portion of the present research program involves repeating and enlarging upon this experiment. During this grant period, the principal investigator has visited in the Institut für Anorganische Chemie und Elecktrochemie at Aachen which is the laboratory that reported the CCl_2 synthesis. These workers now feel that their experimental results are better explained by taking the product substance to be an equimolar solution of chlorine and dichloroacetylene.

During the period of this grant, a comprehensive review by the principal investigator of this little explored field of chemistry was prepared and presented at the Fifth International Symposium on Free Radicals in Uppsala,

Sweden.* This review, which cites well over 300 original literature reports and covers all techniques of chemical synthesis involving these temperatures, served to introduce a half day session on Low Temperature Chemistry as part of the Fifth Symposium. A really good program in chemical synthesis must be capable of using all of these techniques.

Present technology indicates that preparations of concentrated free radicals in amounts useful for propulsion are unlikely. However, the preparation of new compounds which may be highly endothermic, and new forms of known compounds by the techniques of low temperature chemistry are not at all unlikely, but rather, highly probable. It is our belief that new processes for the synthesis of new compounds by these techniques is both possible and feasible. But much research in which a new technology must be developed needs to be done. In addition to the use of these high energy molecules as propellants, studies on such compounds would yield new fundamental information on chemical valency, on molecular structure and particularly on reaction kinetics.

*Copies of this document were sent to NASA on August 25, 1961. The review is also contained in the published book of the proceedings of the conference (6).

II. SPECIFIC PROBLEMS AND RATIONALE DEVELOPED DURING THIS PROGRAM

Succinctly stated, the objectives of this study are to develop sources of carbene and the dihalocarbenes by the pyrolysis of suitable parent substances and to then investigate the chemical stability and reactivity of these species at cryogenic temperatures. As a necessary prerequisite to these studies, the time-of-flight mass spectrometer was to be designed to permit the analysis of samples at cryogenic temperatures without their warm-up prior to ionization.

Molecules containing divalent carbon can be made by a variety of techniques. As was discussed in the previous section, pyrolysis, gaseous discharges, submerged arcs and flames, etc. can and have been used to produce degradation of a parent molecule, the fragments of which may subsequently react in or be trapped by a very low energy environment. In this study we have concentrated on the production of the labile species by thermal decomposition of a suitable parent molecule. The reasons for this were twofold: first, a simple pyrolysis can be made to produce larger quantities of the molecule of interest as compared to some others, for instance, to a photolysis or irradiation technique; and second, the thermal technique, being milder than any other, is least likely to produce random degradation and electronically excited species which characterizes the glow discharge. From the point of view of the low temperature synthesis of useable concentrations of postulated product substances, much depends on the product species having a singlet or a "molecular" ground state. Low molecular weight free radicals have a very low, if not zero, activation energy for recombination and hence they may only be stabilized by diffusional inhibition (1). Such a species is then not to be considered as a chemical reagent.

In the preparation of liquid CCl_2 by the quenching of the gases from the pyrolysis of CCl_4, the pyrolysis was affected at 1300° C in the presence of carbon, and the low temperature quench used liquid air. The carbon to chlorine ratio of the new liquid was found to be 1:1.9 and the molecular weight was determined to be 84.6, comparing favorably with the theoretical value of 82.9 for CCl_2. The material was oxidized by air to phosgene, $COCl_2$. However, the original interpretation has now been retracted in favor of an interpretation based on the assumption of the product being an equimolar mixture of Cl_2 and C_2Cl_2. A mixture of these two compounds exhibits the same properties as noted for the substance quenched from the pyrolysis of CCl_4.

Laidler and Casey (7) have predicted CH_2 to be a singlet with an excitation energy of 19 Kcal to the triplet "diradical" state. Their calculations permit the estimation of the heat of formation CH_2 relative to C(s) and H_2(g) of +172 Kcal. Walsh (8) has, however, reasoned that CH_2 is in a triplet state in which each hydrogen atom is held to the carbon through a carbon sp hybrid atomic orbital. This problem has also been discussed by Lennard-Jones (9), by Pearson, Purcell, and Saigh (10) and by many others. A most significant result is that of Herzberg and Shoosmith who have made the first direct observation of CH_2 (11)*. Subsequent studies by Herzberg have led to a value for the ionization potential of CH_2, 10.396 ev, (11). From a survey of all data on CH_2, it seems apparent that the species is generally produced in an excited singlet state which decays to a triplet ground state only after many collisions (12). These are certainly not encouraging circumstances for the low temperature trapping experiments that have been outlined here.

*It is amusing that although the chemist has been using CH_2 in his arguments about reaction mechanisms for many, many years, it was only in 1959 that the species was finally observed spectroscopically.

III. APPARATUS

A. Mass Spectrometer

Chemical analysis in cryochemical investigations must be performed on the cold substances themselves, and in a manner not allowing warm-up. This results from the fact that the product or effect that is of interest will often only exist as long as the low temperature is maintained. For example, the interesting molecule, ozone difluoride, O_3F_2, begins to decompose above 115° K. Of the many analytical devices that might be used for low temperature analysis (1), we have selected the Bendix time-of-flight mass spectrometer. There were three basic reasons for this choice. First, the output data are simple and easy to understand by persons not experts in specialized areas of modern physics. The reverse of this is true, for example, for the nuclear magnetic resonance and electron spin resonance spectrometer. Secondly, the mass spectrometer will detect all species and not just free radicals as does the electron spin resonance spectrometer. And, thirdly, the Bendix instrument is designed such that it was relatively a simple problem to modify and adapt it for the introduction of a cryogenic sample. The absence of the magnets of a deflection type mass spectrometer makes for an open structure which is readily amenable to the assembly of complex cryogenic dewars and associated apparatus around the ion source. The sample gas must not suffer collisions with any other gaseous molecules or with any surface that is not at ambient temperature prior to its dissociation, ionization and the acceleration of the sample fragments into the analyzer section of the spectrometer. And here ambient temperatures may be as low as 4.2° K. The basic operation of the instrument (13) and the several design modifications which were developed with consultation from the Bendix Corporation engineering and research staff are described below.

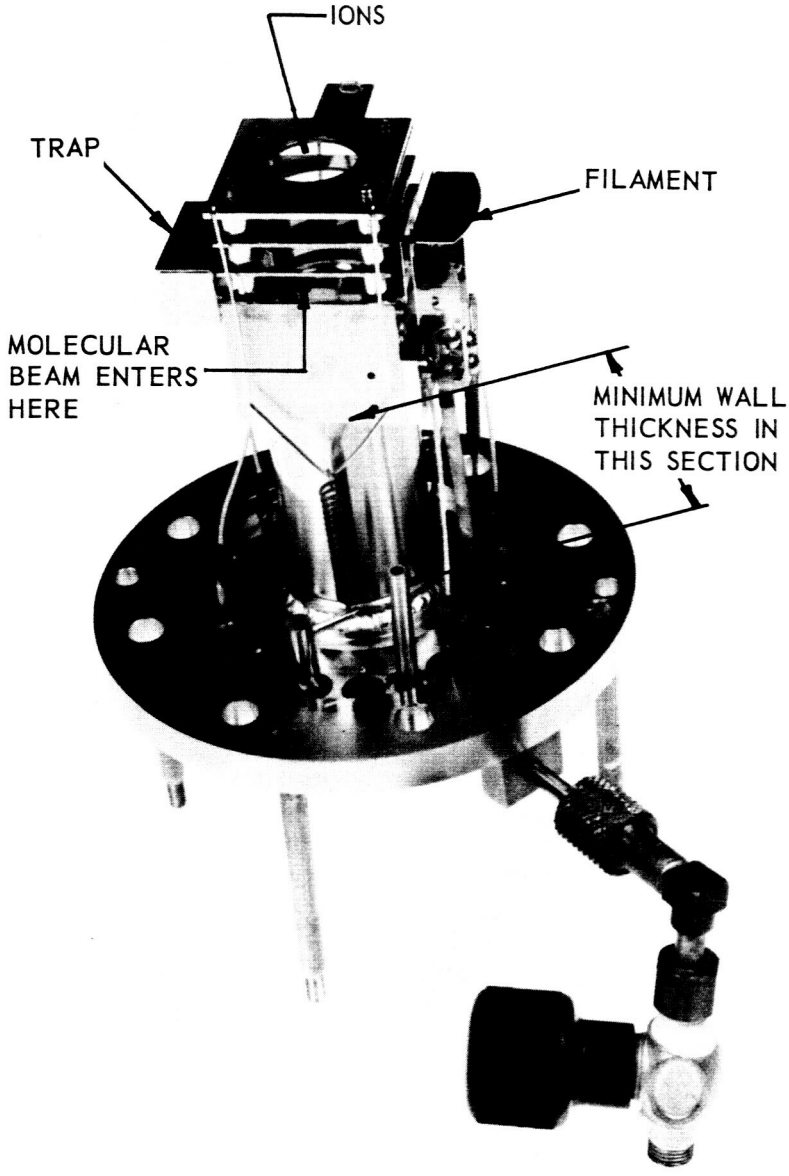


Figure 1. Ion Source of Mass Spectrometer.

The source is built around a re-entrant well on a header (Fig. 1) which mates onto opening (a) of an unsymetrical pipe cross that is shown schematically in Fig. 2.

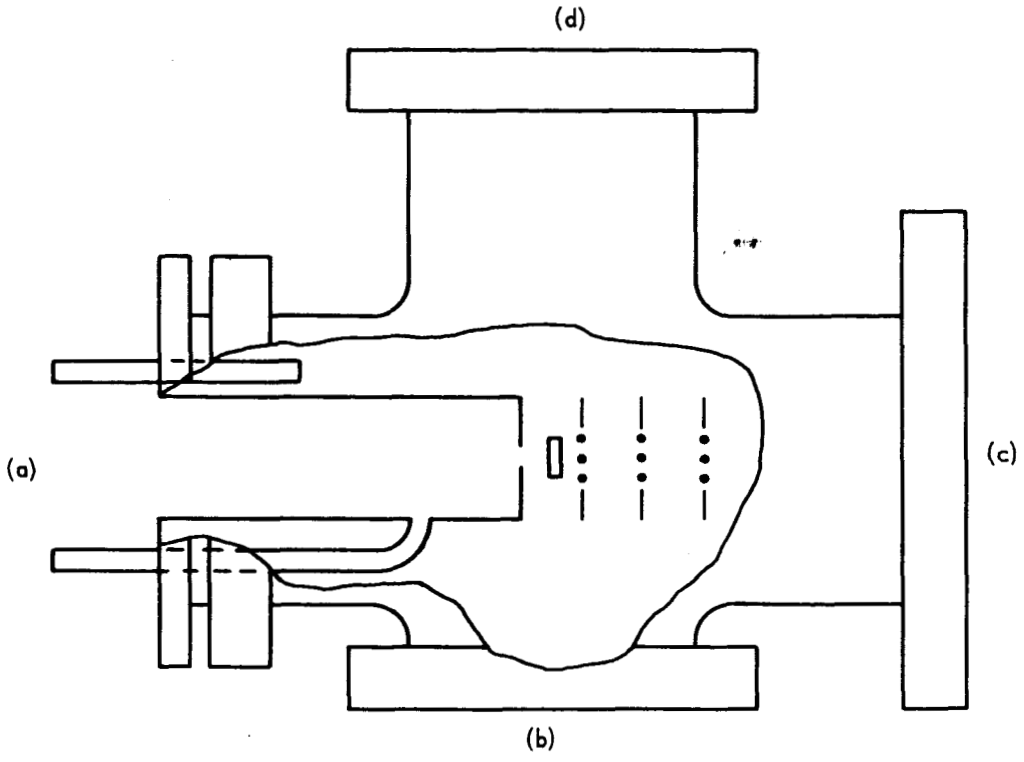


Figure 2. Ion Source and Cross Configuration

The mass spectrometer is pulsed at 10kc and hence 10,000 complete mass spectra are produced per second. The electrons are generated from an internally heated 0.005 in. tungsten wire and are normally kept from entering the ionization chamber by means of a negative bias on a control grid. At the beginning of each cycle, a 0.25 microsecond positive pulse is applied to the control grid, allowing the magnetically collimated electron beam to pass through the ionization

region. This electron beam may be amintained at a constant current while varyint the energy between 0 and 100 volts. During ionization, all elements surrounding the ionization chamber are at ground potential. With the inlet arrangements developed during this NASA program, the sample is either injected as a molecular beam (see Fig. 1); as either an effusive or hydrodynamic flow directly into the ionizing electron beam; or as a simple bleed into the cross for routine analyses. The first two of these will be discussed in some detail subsequently. Immediately after the electron beam is turned off by the control grid, the newly formed ions are pulsed out of the ionization region and given an acceleration of 2800 volts whereon they travel down a 1 meter drift tube to an ion collector and magnetic electron multiplier. Since the ions, although having differing masses, will have the same energy, they will be traveling at different velocities and hence they will separate into mass dependent bunches. The arrival of each bunch at the multiplier produces a signal that is suitably amplified and presented on an oscilloscope and on an oscillograph through an analog output circuitry.

The ion source of the basic spectrometer was somewhat modified to permit its use with cryogenic substances. The ion source modifications allow for (1) a wide open structure on the face shown in Fig. 1 to permit the direct insertion of the cryogenically cooled sample delivery device between the ion grids themselves, and (2) to reduce to a minimum the heat leak into the surfaces that form the ionization space by turning the cyclindrical portion of the reentrant well to a minimum wall thickness and by maximizing its length. The former design feature allows the ionizing electron beam of the spectrometer to make grazing tangential contact with the cold outlet orifice of the low temperature system. The latter design feature allows the ionization chamber itself

to be refrigerated so that collision with the walls will not destroy the sample. With this arrangement, the cryogenically cooled sample delivery system is inserted into the re-entrant well of the ion header (opening (a) of Fig. 2). Because of the especially designed low thermal conductivity walls of the well, the bottom of the well may be cooled with a minimum refrigerant requirement and with a minimum production of objectionable cooling of the header. This latter characteristic, however, is not now being used in deference to configurations wherein the bulk of the ions are formed from molecules that have made no collision with any surface.

B. Traveling Inlet System

Two sample inlet systems have been built into an arrangement which permits their insertion and withdrawal without the necessity of breaking the vacuum in the spectrometer system itself. This feature is convenient for making small changes or adjustments in the inlet systems. One inlet system consists of a furnace and differential pumping arrangement, and the second is the cryogenic inlet arrangement. For the want of a better name, these are here called a "traveling" inlet system.

1. Furnace Beam Inlet System

As a prerequisite to understanding the nature of the quenched products, it is desirable to know exactly what species are coming out of the pyrolysis furnace. Among other things, one would certainly want to adjust the pyrolysis experimental parameters of temperature, pressure, inert diluent or carrier, as well as the parent substance selection itself to give a maximum output of the species of interest, e.g., CF_2. The pyrolysis output gas is the cryogenic input gas.

To this end, the apparatus shown schematically in Fig. 3 has been designed and fabricated. Except for the insertion-withdrawal features, this design is very much like that originally used by Eltenton (14) and subsequently developed by Lossing, et al. (15) (16), Kistiakowsky (17) and Herron and Dibeler (18), and others; and in all of which it has been possible to detect free radicals or short lived intermediates in reactions of various sorts. In essence the experimental arrangement consists of a simple wire wound furnace [3]* provided with a 0.013 in. orifice, one stage of differential pumping and final injection of the sample gas into the ionization chamber of the mass spectrometer in an only moderately well collimated molecular beam. The final inlet port may be either a 0.001, 0.002, or 0.0005 in diameter hole in a 0.001 in. thick disc of gold foil. Calculations indicate that the 0.001 in. port should yield a beam 0.035 in. in diameter at the point of electron bombardment. The 750 l./sec pumping system maintains a low background pressure. The entire furnace assembly is mounted on a 4.5 in. diameter piston that moves in a double O-ring gland [12] into a vacuum lock [9] and finally advances to within 3/16 in. of the ion grids themselves.

In the schematic shown in Fig. 3, the furnace beam assembly that undergoes lateral motion controlled by the screw [11] has been shown in double crosshatching for clarity. The orientation relative to the ion source and cross of Figs. 1 and 2 is such that the cold trap [20] is on the flange marked (d) of Fig. 2, the large gate valve of the inlet arrangement is on the flange marked (b) and the schematic is made as though looking directly at the top of

*Numbers in brackets refer to identification numbers on Figures.

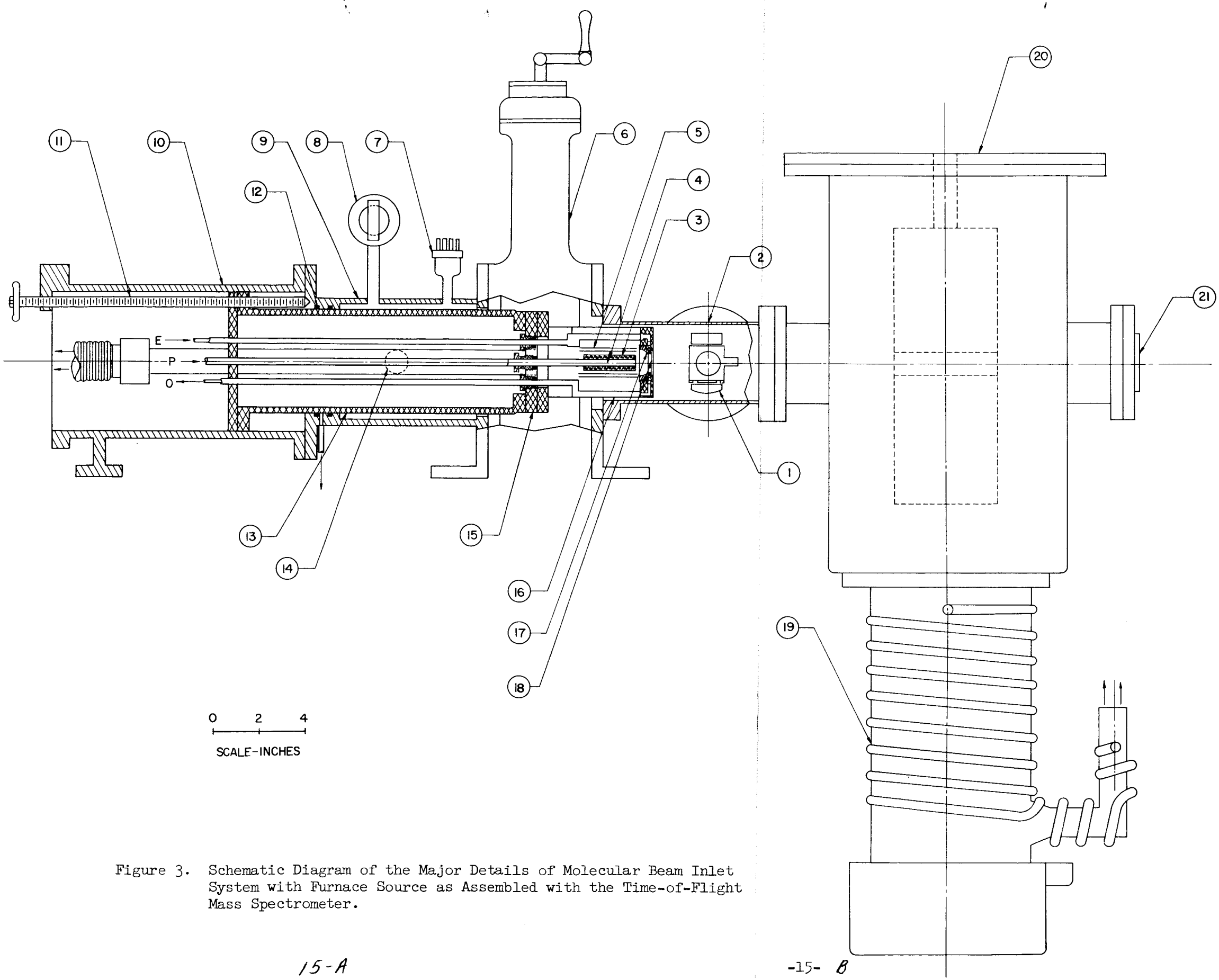


Figure 3. Schematic Diagram of the Major Details of Molecular Beam Inlet System with Furnace Source as Assembled with the Time-of-Flight Mass Spectrometer.

the ion source [1] through the flange marked (c) of Fig. 2.

Fig. 4 is a photograph of the furnace beam assembly when disassembled into its three major components. From left to right these are; the piston assembly; the main header with furnace, radiation shields, etc. mounted; and the differential pumping jacket and cooling assembly. Water is the normal coolant here, but the jacketed tubes allow the use of liquid nitrogen as well. The coolant is circulated to within 3/4 in. of the final slit, which is itself within 15/16 in. of the electron beam of the spectrometer. The furnace tube is heated over 2-1/2 in. and is reasonably uniform in temperature. For example, in one experiment the temperatures were 541°; 555°, and 546° C at 0, 1/2 and 1 inches from the orifice respectively. About 1000° C is the upper operating temperature of this furnace.

The reason for this rather complex mechanical design was to allow the furnace and beam assembly to be withdrawn for minor adjustments without having a complicated disassembly and without having to break up the vacuum in the spectrometer. This latter feature allows the spectrometer to be used in routine analytical work when the furnace and beam assembly is withdrawn, and it also allows one to use the fast reaction inlet of the spectrometer which is coaxial with the ion drift tube and which permits the sample to be injected directly into the electron beam. A second furnace inlet system has been built in which the apparatus fits into this fast reaction re-entrant well of the ion source header. It is described in a later section of this report. In operation, the traveling furnace beam inlet is positioned 3/16 in. away from the front surface shown in the photograph of Fig. 1. Numbering the ion grids from bottom to top as 1, 2, and 3, the beam is ejected between the top of the source base

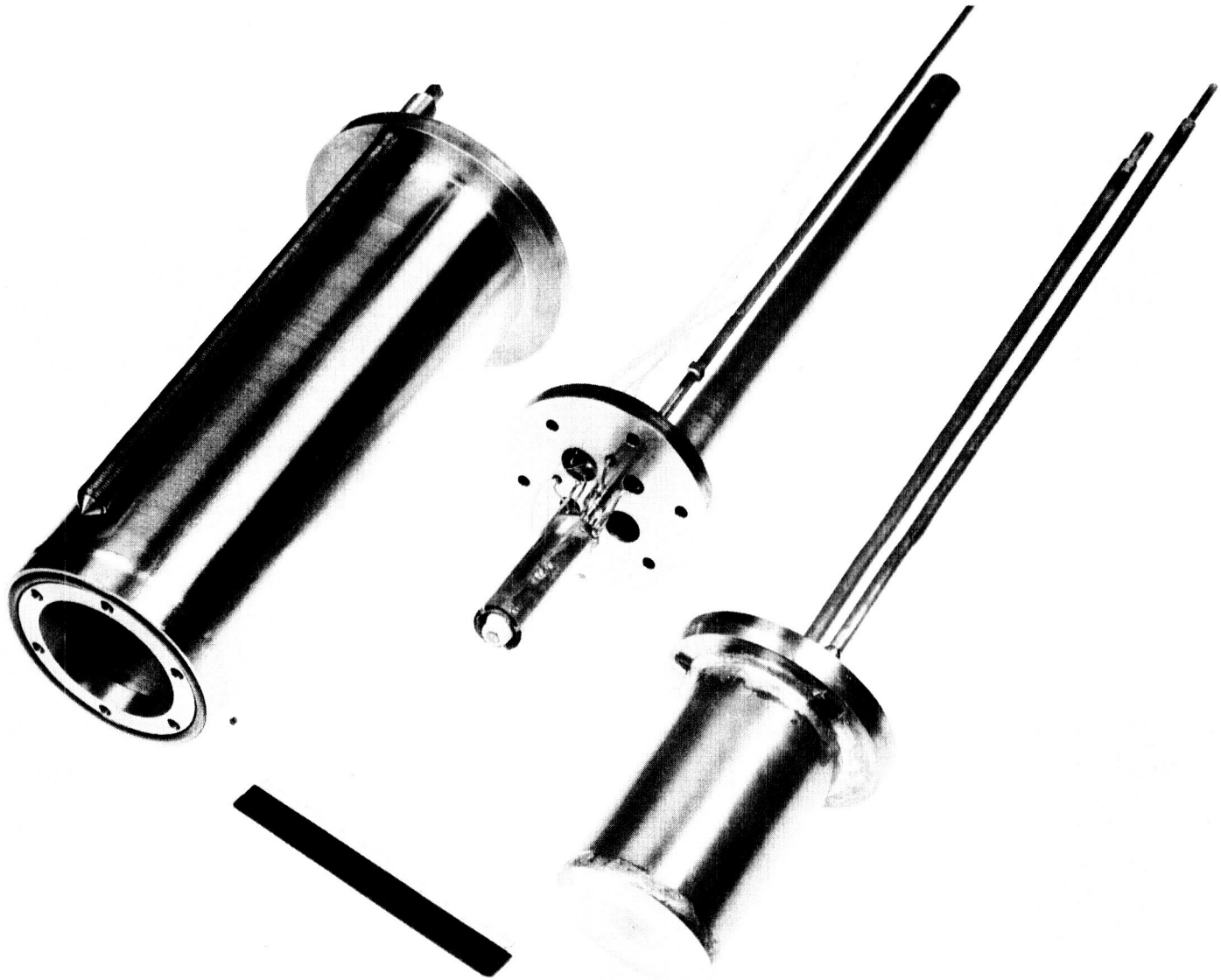


Figure 4. Major Subassemblies of the Furnace Beam Inlet System.

structure and ion grid No. 1. The electrons are pulsed from right to left across the same space, i.e., at right angles to the molecular beam, and the ions are pulsed at right angles to both of these beams, i.e., out of the top of the source assembly. An overall view of the apparatus is presented in the photograph of Fig. 5.

2. Thermal Gradient Freeze-Out and Cryogenic Inlet System

Having then determined the optimum pyrolysis conditions as described above, we must now demonstrate the existence of the species of interest in the condensed phase at cryogenic temperatures. We must also investigate the effect of the concentration of the active species in an inert diluent on that species physical stability and chemical reactivity. The enrichment, or hopefully purification, of the active species is a necessary part of this investigation. These things, as well as the analytical and identification aspects of the total experiment must be performed in ways not involving prior warm-up of the product materials. Absolute temperature control is essential throughout the experiment. In these studies, the apparatus shown schematically in Fig. 6 is being used in an attempt to meet these requirements.

Again the cryogenic assembly is built into a piston which travels in the same O-ring gland, vacuum lock, etc. that were described above, i.e., the double cross-hatched device of Fig. 6 is to now be imagined to be inserted into the apparatus of Fig. 3 in place of the double cross-hatched furnace beam assembly shown there. The unit consists basically of two pots, [5] and [9], which may be independently thermostated at any temperature down to about 60° K. The two L and N Speedomax H, adjustable range, adjustable zero recorder-controllers

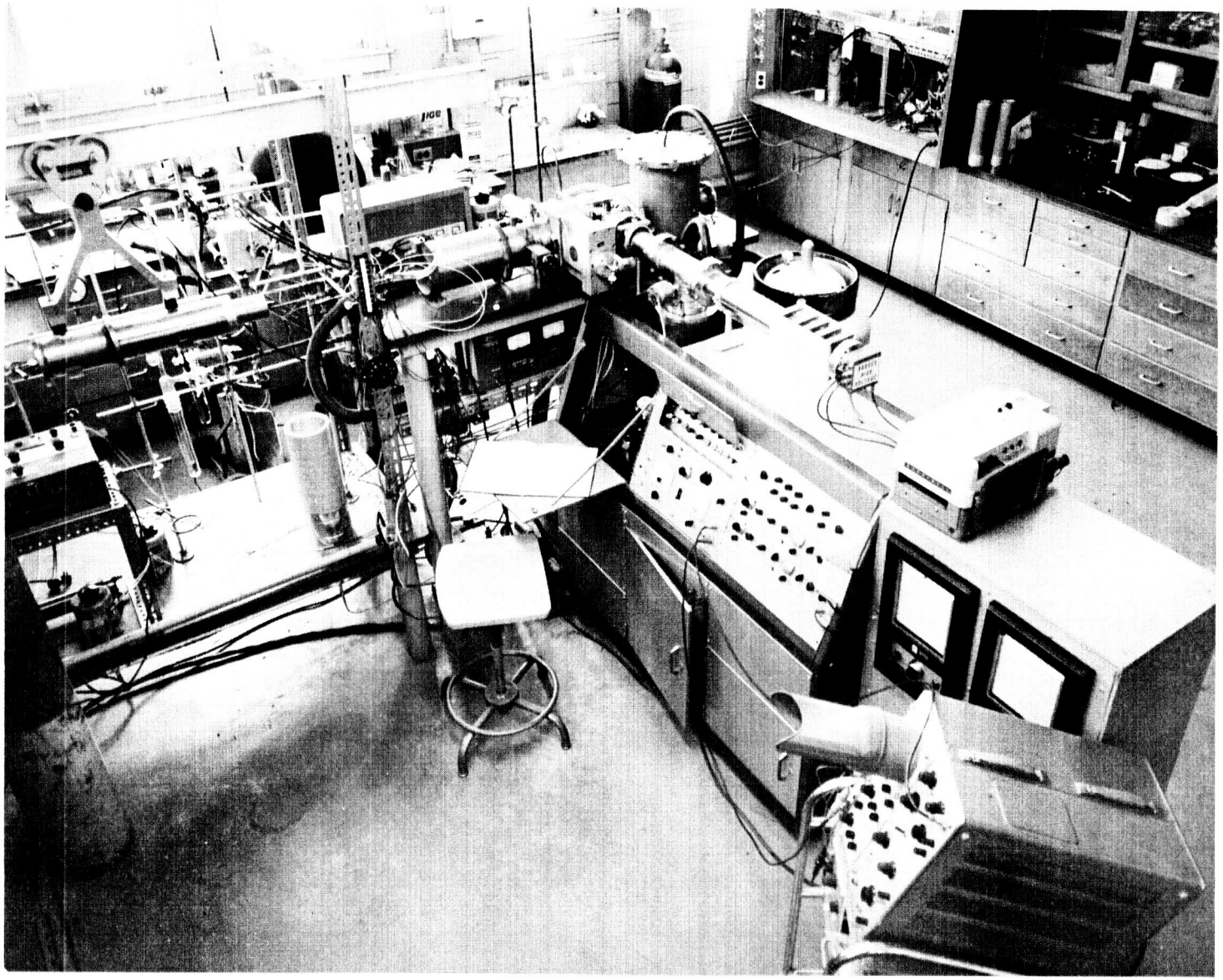


Figure 5. General View of Mass Spectrometer and Associated Equipment.

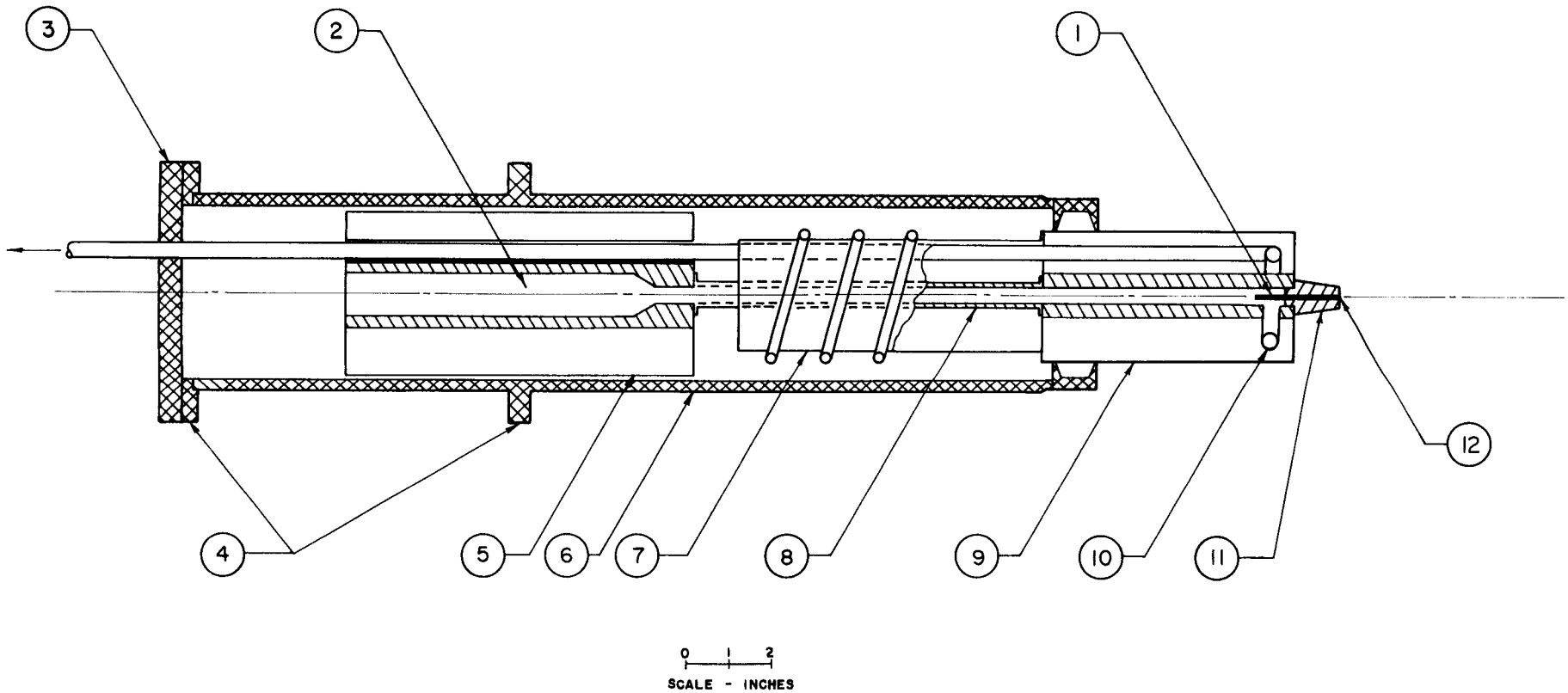


Figure 6. Schematic Diagram of Thermal Gradient Freeze-Out Assembly and Cryogenically Cooled Mass Spectrometer Sample Inlet System.

maintain the constant temperature of each pot. In this arrangement, the controller operates the power to a heater wound on the center tube of each pot which bucks the refrigeration that is continuously supplied by a carefully adjusted input of liquid nitrogen. Obtaining a fixed temperature then is a matter of manually roughly balancing these two counteracting influences, after which the controller will achieve and maintain the balance. With the pots at different temperatures, the connecting tube [8] between these two reservoirs has impressed upon it a thermal gradient which can be made to have any desired slope, $^{o}K/cm$. Every chemist is familiar with the bands of ice that are produced down the walls of a U-tube cold trap when a gas mixture is pumped through it. This effect is pronounced when the dewar around the trap is partially full of refrigerant. This partial separation effect results from the differences in the vapor pressures of the several components. The theory of the gradient tube shown in Fig. 6 is merely to spread out this thermal gradient, to control it, and to take advantage of it as a separation technique. Although made completely of rather massive copper, the outer surfaces of the pots [5], [9]; the gradient tube [8]; and both sides of the radiation shield [7] have been given a heavy nickel plate to minimize this radiative heat leak from the environment. The inner surface of both pots and the gradient tube with which the sample may come into contact have been made chemically inert by sweating in place a 3/8 x 0.010 in. monel tube using pure tin as a solder. Fig. 7 is a photograph of the low temperature pot with the parts displayed in an "exploded" manner. The valve at [10] of Fig. 6 is a 1/4 in. Hoke "flo-mite" ball valve with Ke_1-F seats and teflon packing which has been miniturized to the limit that still preserves the integrity of the valve. The stem is 25 in. long from the ball to the vacuum feed-through on the main header.

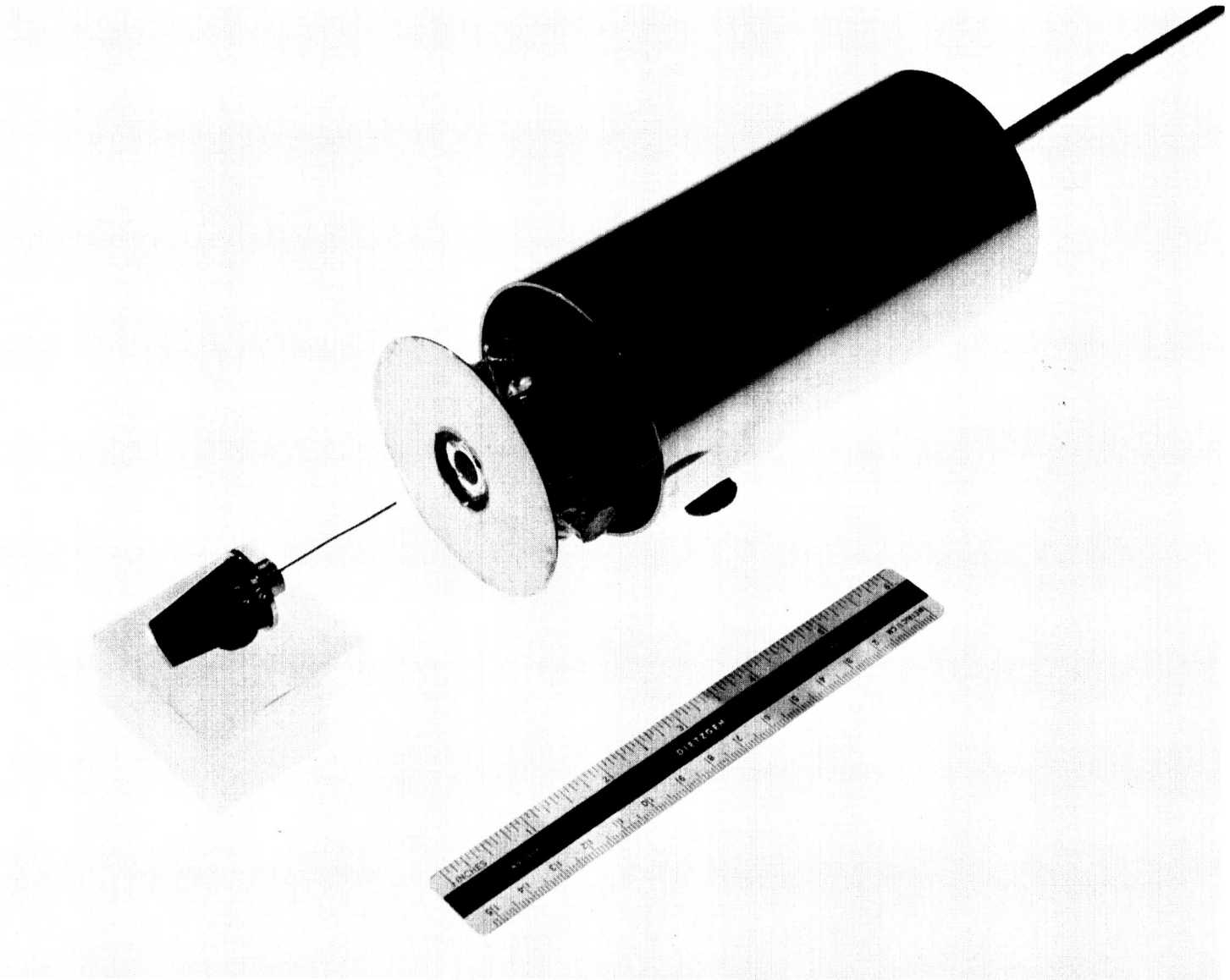


Figure 7. "Exploded" View of Low Temperature End of Cryogenic Purification and Inlet System.

After a time of injecting the effluent from the pyrolysis phase of the experiment into this system (the furnace may be mounted in the large inside diameter of the upper pot), assume that a series of bands of enriched species have been produced in the tube [8]. Now by appropriate manipulations of the temperature of the two pots, first the highest vapor pressure substance, and then the next highest, and so on may be moved down the tube and into the lower temperature pot [9]. This pot or trap has a blade shaped nose [11] which is advanced directly into the ion grid stack between the backing plate and grid No. 1 (see Fig. 1). This blade shaped nose, being made of high thermal conductivity copper, is at essentially the same temperature as is the pot itself (calculation indicates a maximum ΔT of 0.9° K here). The hypodermic delivery tube [1] which is 0.020 in. inside diameter, by 3 in. long, conducts the sample gas from the main volume of the trap into the ionization space of the spectrometer. The exit end of the tube [12] injects the sample directly into the ionizing electron beam since when in operating position, i.e., with the blade in the grid stack, the electron beam makes grazing tangential incidence with this exit port. Again the fast pumping system (750 l/sec) maintains the background spectra at a sufficiently low value. The photograph of Fig. 8 shows the completely assembled device and should be compared with the partially disassembled insert shown in Fig. 4.

The crucial experiments with this arrangement which will verify the stable existence of the dihalocarbenes at cryogenic temperatures have not yet been performed. Such experiments are in progress and will be reported on at a later date. The equipment is not restricted to the dihalocarbenes, but may also be used as a general analytical device in cryochemical studies.

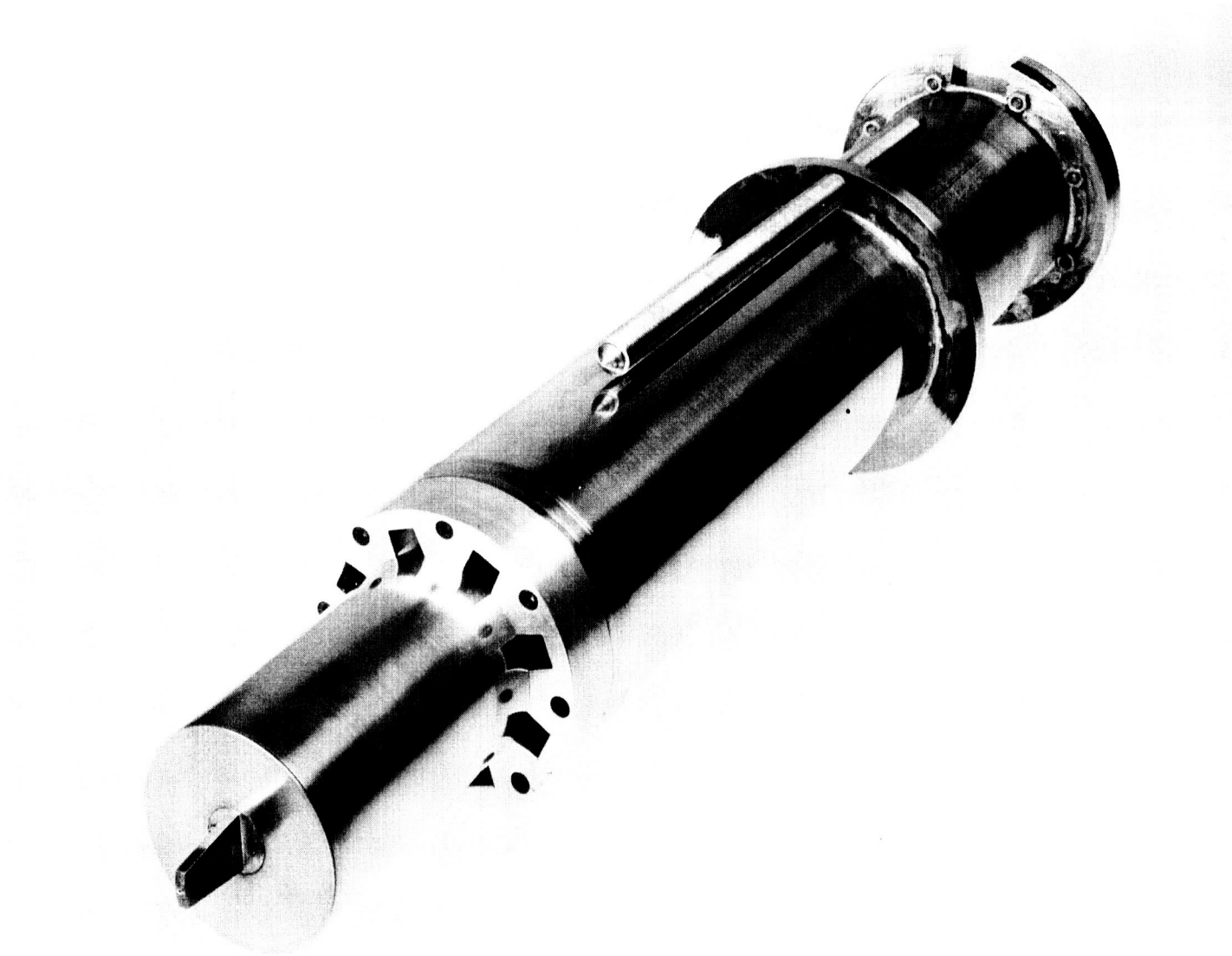


Figure 8. Photograph Showing Overall Appearance of Thermal Gradient Freeze-Out Assembly and Cryogenically Cooled Mass Spectrometer Sample Inlet System.

C. Coaxial Furnace Beam Inlet System

For pyrolysis studies not requiring such high temperatures, it is more convenient to use a much simpler furnace and inlet arrangement which may be mounted coaxilly with the drift tube, inside the re-entrant well on the ion source header. The arrangement developed under this NASA grant is shown schematically in Fig. 9 . In order to study the equilibrium composition of the vapor over C_2I_4 and other easily volatile solids as a function of temperature it was necessary to design an inlet system capable of handling solids. Such a system must include a heating unit to maintain a suitable vapor pressure over the solid parent and a separate furnace to subject the vapor to the desired decomposition temperature. In addition the entire gas handling system must be always at least as warm as the heating unit to prevent the premature condensation of the vapor and consequent lowering of the pressure in the furnace.

The inlet system was constructed so that the outlet of the furnace was within 1/8 in. of the electron beam of the mass spectrometer ion source. The entire system was built as a unit which can be attached to or removed from the spectrometer with a minimum of effort.

The furnace tube itself is made of a copper rod [3] (see Fig. 9) in which three holes were drilled lengthwise. One of these was lined with a monel tube and serves as the heating chamber for the substance being pyrolyzed. It ends in a 0.030 in. outlet. The remaining two holes deadend about 1/8 in. from the outlet end of the furnace and hold an immersion heater [4] and a movable constantan-chromel-P thermocouple, [5]. At 100° C the furnace exhibited a temperature gradient of only 2° C over the 4 inches nearest the spectrometer.

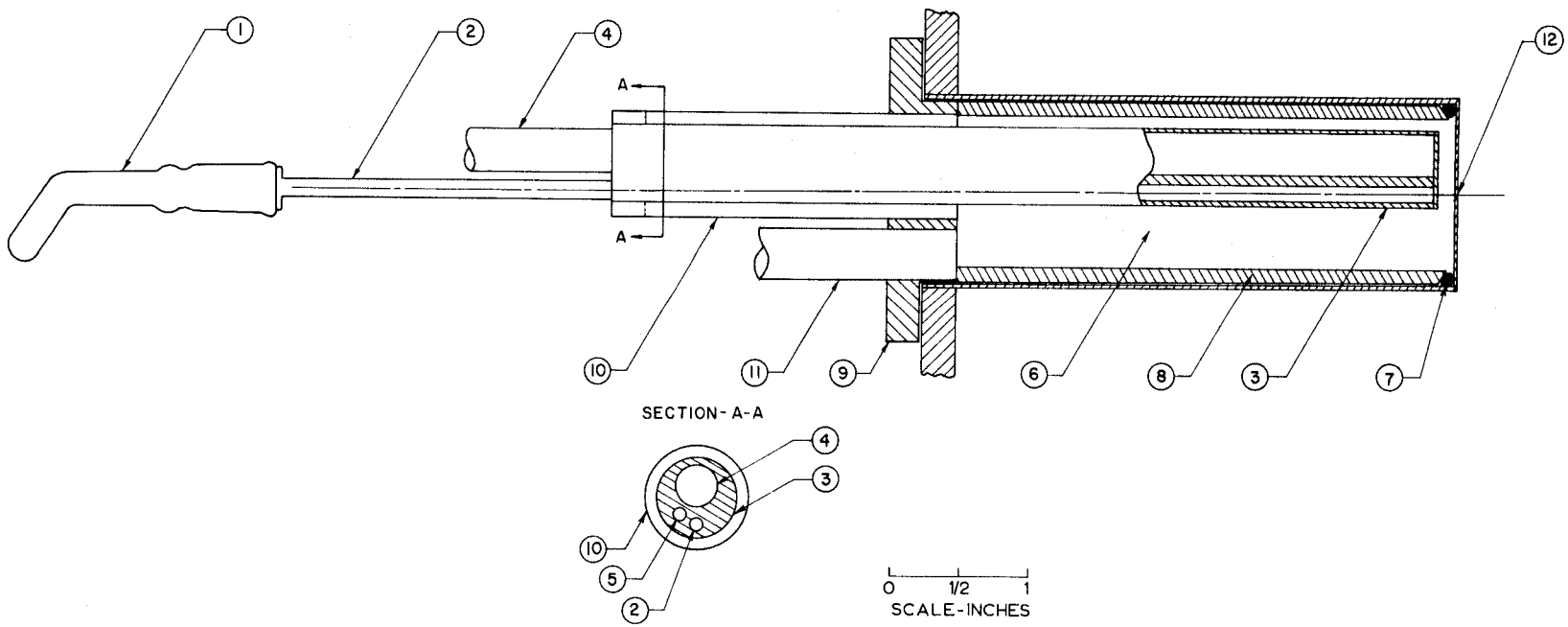


Figure 9. Schematic Diagram of Coaxial Furnace Beam Inlet System.

The furnace was insulated from the header [9] by a thin-walled (0.010 in.) monel standoff tube [10]. The header was designed to bolt directly to the fast reaction inlet of the spectrometer with the vacuum seal made by an aluminum gasket. The fast reaction well [6] thus serves as an intermediate pumping volume and is pumped out through the vacuum line [11].

This intermediate pumping volume is separated from the mass spectrometer by a 0.002 in. pinhole in a 0.001 in. gold foil. The foil is held against the end of the fast reaction chamber by a compression cylinder [8] and a Viton O-ring [7].

The sample is held in the sample tube [1] and both this tube and the delivery tube [2] connecting it to the furnace are heated by a single flexible heating tape.

The same gas handling system that is used in conjunction with the traveling furnace inlet system may be alternately connected onto the coaxial furnace outlet system. This system has been used with the coaxial furnace to study gases which are readily condensed (say with dry ice, 195^{o} K) and in which the sample pressure in the furnace is controlled by controlling the temperature of the sample reservoir immersed in a dewar. The sample pressure is measured with a Consolidated Electrodynamics Corporation micromanometer, model 23-105.

IV. EXPERIMENTAL

A. Verification Studies

Over the convenient temperature range of 400° to 600° K and at 100 microns of mercury pressure, the equilibrium,

$$NO_2 \leftrightarrows NO + 1/2\ O_2 ,$$

varies from practically all NO_2 to all NO. This, therefore, seemed to be an appropriate test system to verify that the two furnace beam inlet systems were operating according to design expectations.

To prove that the samples ionized in the spectrometer are actually identical in composition to those decomposed and assumed to be at equilibrium in the two furnaces, it will be necessary to check each of them with a substance which decomposes in a typical temperature range and whose equilibrium composition is known as a function of temperature. If this known equilibrium is not experimentally reproduced, design modifications will be necessary. For this purpose the system $NO\text{-}NO_2$ was selected for study.

Several experiments utilizing the coaxial beam inlet have been conducted and although the pressure measurement and control has been rather crude, the experimentally determined equilibrium constants agreed surprisingly well with the literature values. Several experimental points are shown in Table I along with the values calculated from the thermodynamic data given by Kelley (19). The pressure in the furnace during these several studies was equilibrated between 130 and 240 microns as indicated by a Consolidated Electrodynamics Corporation micromanometer (Model 23-105).

The sensitivity of the total analytical system to NO_2 was determined with the furnace at room temperature and based on the NO_2^+ peak. At elevated temperatures, the measured NO_2^+ peak height could then be converted to a partial pressure of NO_2 in the furnace. The difference between this partial pressure and the total pressure when multiplied by 2/3 was taken to be the partial pressure of NO in the furnace.

TABLE I

COMPARISON OF EXPERIMENTAL AND THERMODYNAMIC EQUILIBRIUM CONSTANTS FOR THE DISSOCIATION OF NO_2

Temperature (^oK)	$K_{experimental}$	$K_{thermodynamic}$ (19)
444	1.0×10^{-3}	1.53×10^{-3}
473	6.1×10^{-3}	3.9×10^{-3}
473	3.1×10^{-3}	3.9×10^{-3}
510	6.7×10^{-3}	1.16×10^{-2}
535	8.3×10^{-2}	2.22×10^{-2}

These data may be improved by better pressure regulation in the furnace. The most likely non-instrumental source of error is in the possible nonequilibrium of the reaction itself. The NO_2 dissociation is known to be rather slow. Better experiments utilizing a packed bed of catalyst (activated charcoal) in the furnace will lead to better results. However, it certainly seems that the coaxial inlet system is operating according to design expectations. Similar verification studies with the "traveling" furnace beam inlet have not yet been successfully performed due to recurring vacuum troubles.

B. CI_2 Production

As stated earlier, one of the primary objectives of this study has been to develop sources of the dihalocarbenes, the reactivity of which is then to be observed at cryogenic temperatures.

The pyrolysis of C_2I_4 using the coaxial furnace and beam inlet system was studied. It was found that this solid parent substance had to be heated to at least 100° C to give a vapor pressure sufficient to produce a suitable spectrum. An examination of the equilibrium vapor of the C_2I_4 at various temperatures from 100°-300° C showed that, at these moderate temperatures, the C_2I_4 decomposed into C_2I_2 and I_2 rather than the desired CI_2.

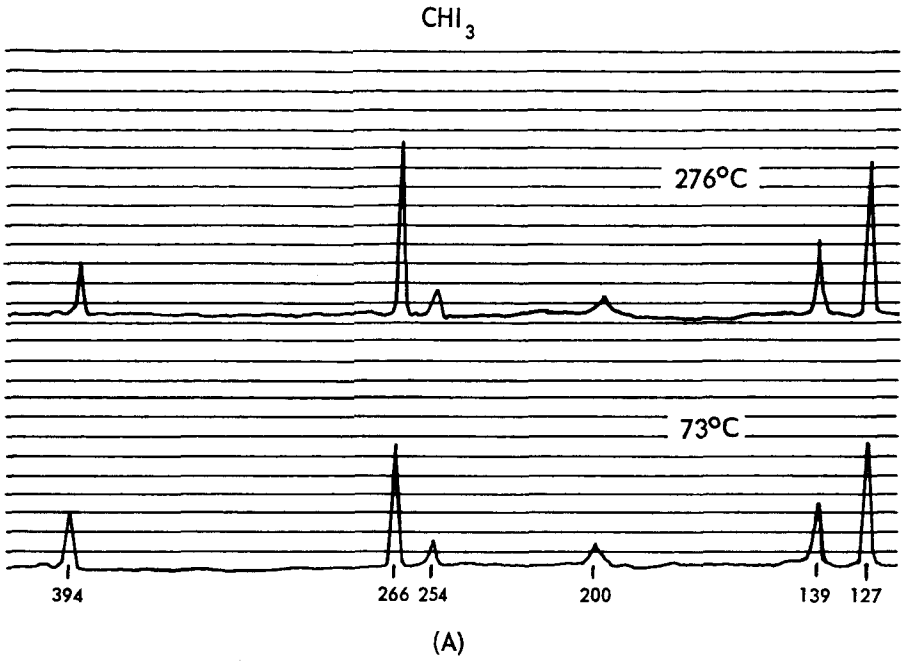
Experiments on the pyrolysis of CHI_3 can be interpreted to indicate that a considerable amount of CI_2 is present in the pyrolysis products at moderate temperatures (below 300° C). There are some uncertainties in the interpretation of this data due to the difficulty of resolving adjacent mass peaks at the high mass numbers of the heavy iodine compounds. The peaks corresponding to CHI_2^+ ions and to CI_2^+ ions still remain to be completely resolved but a small shoulder on the high mass side of the main peak leads us to believe that CI_2^+ is the main contributor to this peak (see e.g. Fig. 10b).

The data in Table II show the large increase in the CI_2^+ or CHI_2^+ ion current relative to that of CHI_3^+ or CI_3^+ with increased temperature.

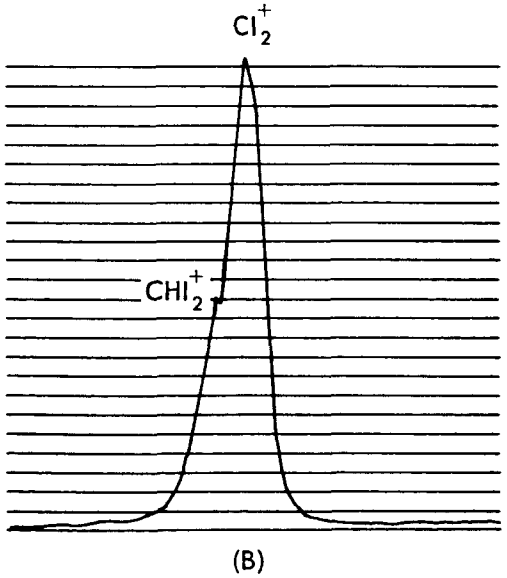
TABLE II

CI_2^+/CHI_3^+ RATIO AS A FUNCTION OF TEMPERATURE, (50 VOLT ELECTRONS)

T(°C)	CI_2^+/CHI_3^+
73	100/42
117	100/40
146	100/43
276	100/32



(A)



(B)

Figure 10. (A) Mass Spectrum of CHI_3 at Two Temperatures Showing Effect of Pyrolysis. (B) Detailed Trace of CI_2^+ and CHI_2^+ Peaks.

This effect is best explained as resulting from the formation of CI_2 in the furnace causing more CI_2^+ ions to be formed by an ionizing electron beam of fixed current and fixed energy. This statement assumes that the cross sections for the various processes involved, such as,

$$CI_2 + e \rightarrow CI_2^+ + 2e ,$$
$$CHI_3 + e \rightarrow CHI_3^+ + 2e ,$$
$$CHI_3 + e \rightarrow CI_2 + (\text{other products}) ,$$

do not change significantly with temperature up to about 300° C, which was the maximum furnace temperature used in these studies. This also assumes that no vibrational or other excitation of any of the species is contributing to form a reduced energy requirement for any process. Interestingly, CHI_3 is known to explode upon heating to temperatures of 210° C or above(20).

Further experiments are being performed to verify that this peak is due to CI_2^+. If this proves to be true, optimum conditions of temperature and pressure, consistent with our apparatus, will be determined for the production of CI_2. Then trapping experiments will be performed in an effort to isolate CI_2 at cryogenic temperatures. It is anticipated that these trapping studies will initially involve matrix isolation of the labile species, followed by a study of the stability (or reactivity) of the species as the ratio of the inert matrix to active material approaches zero.

C. CF_2 Production

Apparently a good parent substance for the production of CF_2 is tetrafluoroethylene, (TFE). C_2F_4 is an obnoxious material in that it is subject to

violent decomposition under certain poorly defined conditions, so that it must be handled with extreme care. With this precaution, the substance is being prepared for this study by the thermal degradation of teflon and purified by simple bulb to bulb distillation (22). Helpful information on the production, properties, storage and handling of TFE was obtained from the du Pont Company in their bulletin, "Safe Handling of Tetrafluoroethylene," but neither they nor any other vendor who was contacted would sell a sample of the material. C_2F_4, together with Genetron-1113, chlorotrifluoroethylene, C_2ClF_3, are to be used as parent substances in pyrolysis experiments very similar to those just described for the production of CI_2. These experiments are in progress, but are not sufficiently developed for inclusion in this report. The results will be published at a later date.

Still a third source of CF_2 that has been developed within the last year (23) is the pyrolysis of $P(CF_3)_3F_2$ which is reduced in a stepwise fashion all the way to PF_5, i.e.,

$$P(CF_3)_3F_2 \rightarrow P(CF_3)_2F_3 + CF_2 .$$

According to Mahler, who discovered this process, the parent compound is made by the reaction of SF_4 with $(CF_3)_3P$ at 25° C. In the absence of other reactants, the CF_2 disappears irreversibly by forming the dimer, trimer, or polymer. Decomposition of the $P(CF_3)_3F_2$ occurs very slowly (0.5 percent per month) in the gas phase at 25° C.

An encouraging fact from the point of view of the CF_2 quenching experiment may be inferred from the trapping experiments of Mastrangelo (24). In these experiments, C_2F_6 and cyclo- C_4F_8 where subjected to a Tesla coil leak

detector discharge and immediately frozen onto a 77° K surface. Red and blue deposits were formed which were ascribed to trapped CF_3 and CF_2 radicals respectively. This deduction was based on analyses of the room temperature gases from such an experiment when either of several reactants was deposited on top of the red or blue material prior to the warm-up of the composite mass. Since no low temperature data were obtained, these deductions had to be inferred indirectly from room temperature information.

D. $CC\ell_2$, CBr_2 and CH_2 Production

No significant results may be reported on these species at the present time. The studies are continuing and the results will be published at a later date.

E. Ionization Energy Measurements

In understanding the chemistry of unusual molecules at cryogenic temperatures it is important to have accurate knowledge of bond strengths. It is also important to have a qualitative "feel" for bond strengths and activation energies that are not now known. Both of these objectives can be met by a continuing study of the chemistry of these low temperature species with guidance from the best of current theory.

Experimentally observed ionization potentials are thought to provide the most reliable basis for evaluation of molecular orbital calculations (25), and hence it should be of interest to compare various semi-empirical and theoretical molecular orbital methods with experimental results for several compounds that are of interest here. Hall (26) has presented such a comparison for methyl and chloro-substituted ethylenes. The strength of chemical bonds can

also be estimated from appearance potentials if certain other information can be observed or calculated. Such bond strength information is important for the understanding of chemical kinetics.

The time-of-flight mass spectrometer may be used in several ways to obtain appearance potentials with various degrees of accuracy. A very rapid method has been developed by Kiser and Gallegos which is claimed to be accurate to $\pm$ 0.2 volts (27). The gas under study and a calibrating gas are admitted to the spectrometer simultaneously and their peak heights as obtained with an electron energy of 50 volts are recorded. Then, the sensitivity of the spectrometer is increased 100-fold and the electron energy decreased until the ion current is the same as for 50 electrons. The difference in the voltages obtained is taken as the difference in ionization potential of the gas under study and the calibrating gas. This method has been tried in this laboratory and results have proved to be about as accurate as was claimed for this procedure.

The more usual method of obtaining ionization potentials with the mass spectrometer is by the use of ionization efficiency curves. Many of these mass spectrometer methods for determining ionization potentials have been summarized by McDowell (28). These plots of ion intensity vs. electron energy may be made to approach the true ionization potential very closely by using the method of Fox, et al. (29). A retarding potential is applied to the electron beam to yield an energy distribution with a sharp low-energy limit. By varying the retarding potential slightly, a new low-energy limit is selected. The difference in ionization is due to the electrons with energies between these two lower energies. By varying the potential in very small steps, the ionization efficiency curve may be plotted very accurately. This procedure is commonly known as the retarding potential difference (RPD) method.

The acquisition of the necessary additional equipment needed for use with the RPD technique is underway. The arrangement used here will be similar to that described by White, et al. in their Knudsen cell work (30).

F. Synthesis of Oxygen Fluorides

The substances, O_3F_2 and O_2F_2 are typical of the compounds that are being synthesized in this program insofar as these compounds are thermally unstable at still very low temperatures. O_3F_2 decomposes rapidly above 115° K and O_2F_2 above 200° K (2). To study these substances in the cryogenic inlet system described above would serve to verify that the inlet will function as designed, i.e., in cold in situ mass spectrometric analysis; and in addition, the results would be interesting in their own right since little of the properties of these very interesting compounds is now known.

With these objectives, the oxygen fluorides were produced using a glow discharge reactor in which the discharge tube is immersed in liquid oxygen. A diagram of the gas handling system and reactor is shown in Fig. 11. The fluorine cylinder and four control valves shown inside dashed lines is meant to indicate that this part of the system was assembled inside a barricade with remote valving using extended valve stems. This is standard safety procedure with high pressure elemental fluorine. A15 KV neon sign transformer controlled by a variac in the primary, together with a variable series limiting resistor in the secondary permitted satisfactory control of the power to the reactor. After passivating the inner surfaces of all units and interconnecting tubing (1/4 X 0.035 in. copper tubing with swagelok fittings and brass bellows type valves), a mixture of O_2 and F_2 gas was prepared in the 16ℓ stainless steel vessel [V] using the mercury manometer [M]. The reactor was immersed

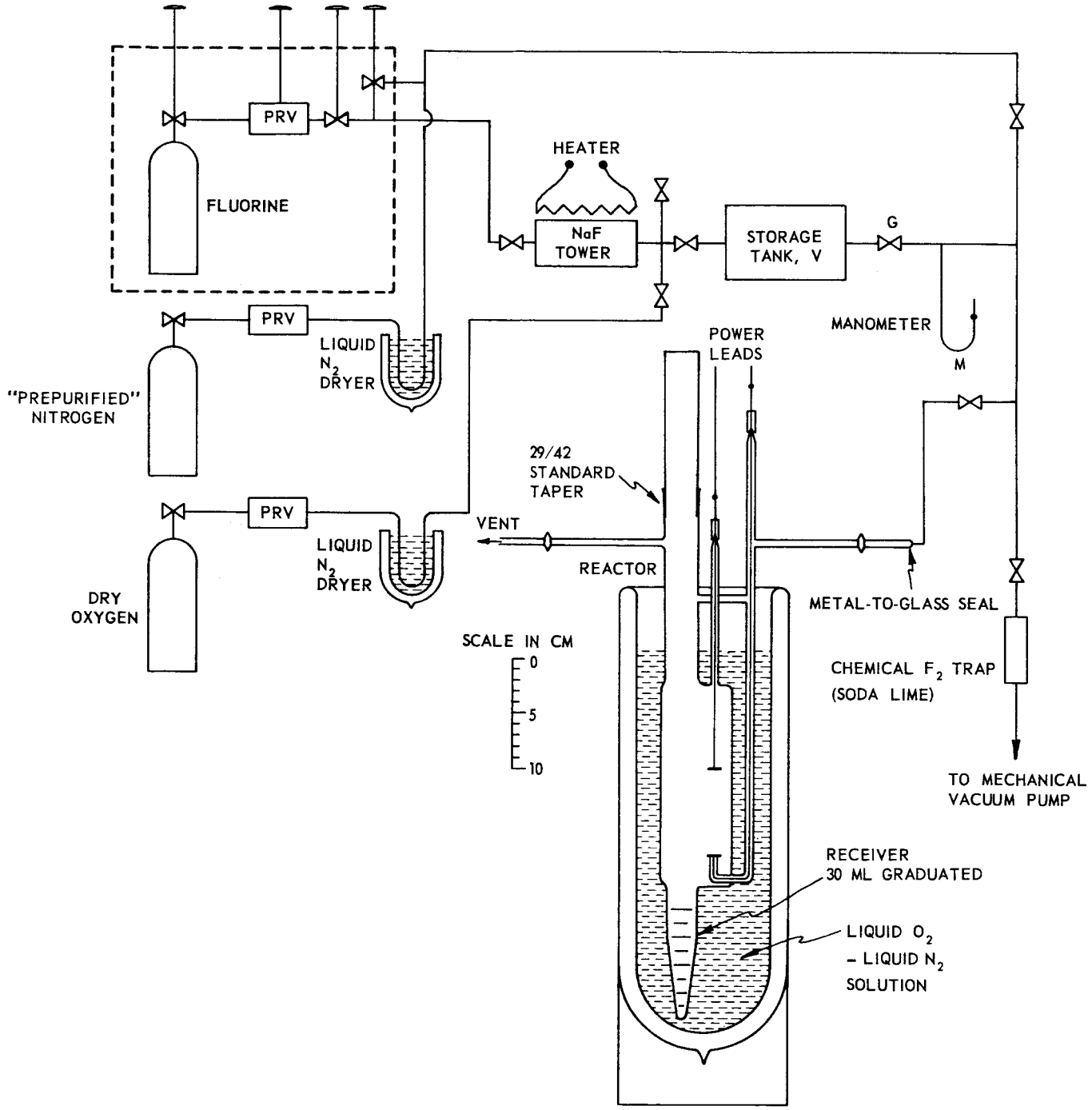


Figure 11. Schematic Diagram of Oxygen Fluorides Synthesis Apparatus.

in a solution of liquid oxygen containing some nitrogen so as to give a thermostated temperature of 83^{o} K. The mixed gases, in stoichiometric proportion were then admitted to the reactor and the discharge was ignited. A brass Whitey micro-regulating valve [G], type 2RS4, was used quite satisfactorily as a flow regulator to maintain the reactant input rate at very nearly the product production rate. This was apparent from the stability of the reactor pressure as monitored by the sulphuric acid manometer [N]. In a typical run at pressures of 70 - 130 mm acid, i.e., 9 to 18 mm mercury, and a discharge voltage of 3400 to 3800 volts, the reactor gave 1.5 ml of mixed O_3F_2 and O_2F_2 product in 4-1/2 hours. This is much lower than yields of as much as 14 ml per hour that were reported by Amster, et al. (31) and similar high yields reported by others. The low yield was probably due to insufficient cooling of the electrodes and to poor mixing of the input gas mixture. There has been no attempt here to maximize the yield since the need is only for quantities sufficient for mass spectrometer analysis and that is readily met by these much smaller quantities.

The transfer pipette for transferring a sample from the reactor to this cryogenically cooled inlet of the mass spectrometer is inserted through the 29/42 standard taper on top of the reactor.

V. CONCLUSIONS

The primary requirement for meaningful research in low temperature chemistry is that of cold chemical analysis. The species and phenomena that are being observed must be observed at the low temperature since warming will usually destroy, or at best, greatly complicate the experiment. This requirement has been met in these studies by modification of the Bendix time-of-flight mass spectrometer and the design and construction of a unique cryogenically cooled inlet system. In essence, the sample container, at the very low temperature, is positioned such that the molecules immerging from a pin hole in the container are instantly in the path of the ionizing beam of the spectrometer.

Purification, or at least some enrichment of the interesting product species, is also necessary. Here again, the enrichment processes of whatever sort, must be conducted in such a manner that the product mixture is not warmed to a temperature at which some constituent might become either physically unstable or chemically too reactive to handle. This second requirement has been met in these studies by developing the technique of fractional freeze-out and fractional sublimation. This process is not greatly efficient, but it is simple, which seemed to be the more desirable attribute. Sophistication of these techniques can come later.

The fractional freeze-out assembly and the cryogenic mass spectrometer inlet assembly may be combined if convenient for some particular experiment.

Sufficient study of the arrangement has not been made to allow a final assessment of its utility. It is being examined using the O_3F_2-O_2F_2 system as a "test case", and the results will be published later.

Very few reactions will proceed at cryogenic temperatures by merely contacting the precooled reactants. Usually some form of activation is required. In these studies particular emphasis has been placed on the pyrolysis of a suitable parent to produce the species of interest. Since it is necessary to adjust the pyrolysis parameters of temperature, pressure, flow rate, etc., for optimum production of the species of interest, it is necessary to examine the nature of the effluent from the high energy genesis phase of the experiment. To meet this requirement, two molecular beam inlet systems have been constructed for use with the mass spectrometer. Each has its peculiar advantages and disadvantages. The design operation of one of these systems, the coaxial beam system, has been demonstrated by an examination of the NO_2 dissociative equilibrium.

Several parent substances for the production of the dihalocarbenes have been obtained, but only for CI_2 are the data sufficiently developed to permit a choice of a satisfactory parent substance.

There have been no quenching experiments with any of the carbenes, so the question of their existence is still unanswered. The work is continuing and additional results will be forwarded to NASA as reasonable units of information are developed.

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